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ORIGINAL ARTICLE

# Contact Lenses Wettability *In Vitro*: Effect of Surface-Active Ingredients

Meng C. Lin\* and Tatyana F. Svitova†

## ABSTRACT

**Purpose.** To investigate the release of surface-active agents (surfactants) from unworn soft contact lenses (SCLs) and their influence on the lens surface wettability *in vitro*.

**Methods.** Surface tension (ST) of blister pack solutions was measured by pendant-drop technique. STs at the air-aqueous interface and contact angles (CAs) of four conventional and seven silicone hydrogel SCLs were evaluated in a dynamic-cycling regime using a modified captive-bubble tensiometer-goniometer. Measurements were performed immediately after removal from blister packs, and after soaking in a glass vial filled with a surfactant-free solution, which was replaced daily for 1 week. Lens surface wettability was expressed as adhesion energy according to Young equation.

**Results.** STs of all blister pack solutions were lower than the reference ST of pure water (72.5 mN/m), indicating the presence of surfactants. When lenses were depleted of surfactants by soaking, the STs for all studied lenses and advancing CAs of selected lenses increased ( $p < 0.001$ ). Receding CAs of all studied lenses were  $12^\circ \pm 5^\circ$  and were not affected by the presence of surfactants. For most of the conventional lenses, the surface wettability was largely dependent on surfactants, and reduced significantly after surfactant depletion. In contrast, most silicone hydrogel lenses exhibited stable and self-sustained surface wettability *in vitro*.

**Conclusions.** The manufacturer-added surfactants affected wetting properties of all studied SCLs, although to different degrees.

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Key Words: soft contact lenses, surface wettability, dynamic contact angles, aqueous adhesion energy

Stability and uniform coverage of the corneal surface by the tear film are important factors in maintaining good ocular health. The ocular tear film is a highly dynamic and complex biological system operating under stresses induced by eyelid movement during blinking. A model has been proposed to explain the relationships among tear break-up time and fluid-film physical properties such as viscosity, surface tension (ST), meniscus radius, and initial and final film thicknesses.<sup>1</sup> This model suggests that the tear film is destined to rupture through evaporative film thinning and/or inherent hydrodynamic instabilities. Insertion of a contact lens onto an eye divides the tear film into two thinner parts—the prelens and postlens tear films. A thinner fluid film is more susceptible to spontaneous rupture<sup>1–4</sup>; this has important clinical implications because fast tear-film break-up has been linked to discomfort during contact lens wear.<sup>5</sup>

Effective and full tear-film recovery is believed to depend on the wettability of the ocular surface<sup>6–8</sup> or, in the case of contact lenses, on the lens surface-wetting properties.<sup>9–14</sup> As a result, the contact lens industry has invested significant research effort into developing a soft lens surface that is highly wettable in the ocular environment. In general, several approaches can be used to enhance surface wettability. The traditional approach developed first for conventional hydrogels of HEMA copolymers lenses is to add surface-active wetting agents into lens packaging or lens care solutions. Wetting agents adsorbed on the lens surface are expected to improve the wettability of the lens surface. However, these surfactants can also penetrate into a lens matrix, and it is conceivable that they could also leach out during lens wear. Furthermore, the clinical benefits of this approach have not yet been carefully investigated. The techniques used more recently for silicone hydrogel (SiH) lenses are either plasma surface oxidation (e.g., PureVision and Focus Night&Day) or introduction of a hydrophilic co-polymer into the lens material (e.g., Acuvue Advance, Acuvue Oasys).

The most widely used method to characterize the wettability of a solid surface is to measure contact angles (CAs). It is commonly

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believed that the wetting behavior of a soft contact lens (SCL) surface as assessed by CA measurement can predict the performance of the contact lens *in vivo*: the lower the CA, the better the wettability of the lens surface, and thus the greater the stability of the tear film spread over the lens surface. The cosine of the CA of a liquid drop resting on a solid surface and in equilibrium with a surrounding vapor (gas phase) is determined by Young equation<sup>15</sup>:

$$\cos \theta_e = (\gamma_{sv} - \gamma_{sl})/\gamma_{lv} \quad (1)$$

where  $\theta_e$  is the equilibrium CA, and  $\gamma_{sv}$ ,  $\gamma_{sl}$ , are the interfacial tensions between the solid and the vapor, and the solid and the liquid, respectively, and  $\gamma_{lv}$  is the ST of the liquid. The expression in parenthesis,  $(\gamma_{sv} - \gamma_{sl})$ , is a specific property of a solid-liquid interface and is usually referred to as adhesion tension or adhesion energy; it characterizes the propensity of a liquid attraction toward a solid. When the liquid wets the solid surface completely (i.e., spreads spontaneously over the solid surface and forms a thermodynamically stable film with 0 CA), the adhesion energy is numerically equal to the ST of the spreading liquid, which is 72.4 mN/m for pure water at the room temperature. CAs alone, as one can see from Young Eq. 1, do not provide a true estimate of surface wettability unless the ST of the liquid is taken into account. Lack of ST measurements has led to controversial and inconsistent claims about the CAs of SCLs in the literature. Furthermore, the resolution of the controversies in CA measurements is further complicated by different measurement techniques and/or different media in which measurements were made.<sup>11–14,16–18</sup>

In contrast to most published studies in which static CA measurements (i.e., measurements taken at rest, using the sessile drop technique for advancing, and the captive bubble technique for both advancing and receding CAs)<sup>11–14,16–18</sup> were taken on a small portion of a SCL surface, this study focused on wettability dynamics when CA measurements were taken over a relatively large surface (up to 3/4 of the total area of a SCL). We modified the captive-bubble method<sup>19,20</sup> to systematically study the advancing (corresponding to a film recovery process) and receding (corresponding to a film break-up) CAs on conventional hydrogels and

SiH lenses under dynamic-cycling conditions mimicking blinking cycles. In our experiments, the three-phase contact line, that is, the boundary among lens, air bubble, and aqueous phase, was repeatedly moved along most of the lens surface.<sup>19,21</sup> We also used the modified captive-bubble technique to concurrently measure the ST at the aqueous-air interface. With this new experimental approach of simultaneous CA and ST measurements, we aimed to systematically characterize the surface wettability of several conventional hydrogels and SiH lenses using adhesion energy as a universal, physically meaningful measure of surface wettability. The knowledge gained from these experiments will provide new insights into the mechanisms that determine contact lens surface wettability under dynamic conditions *in vitro*.

## MATERIALS AND METHODS

### Lens Materials

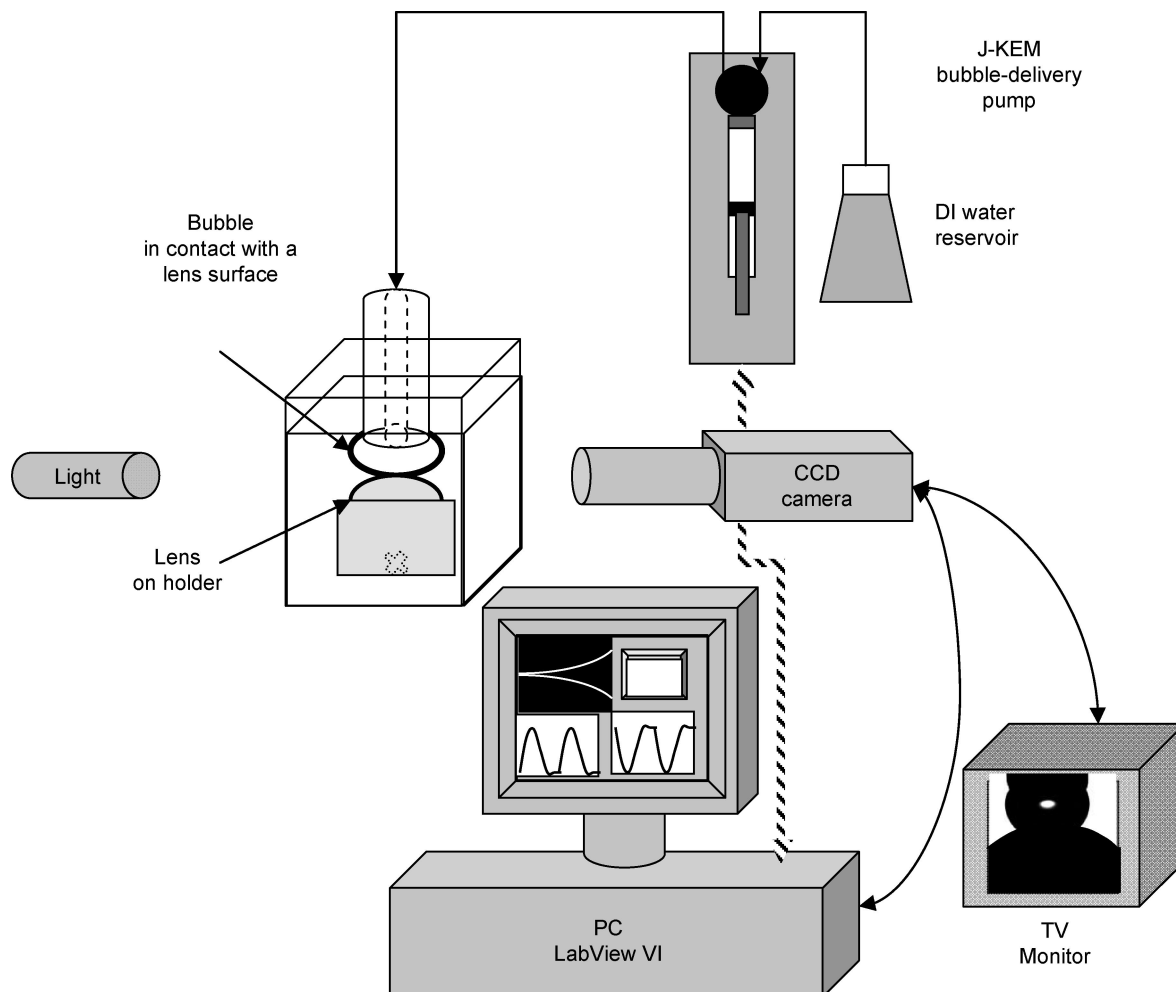
The brands of contact lenses and their specifications as listed by manufacturers are shown in Table 1.

### Surface Tension Measurements

ST measurements were performed using Krüss DSA100 tensiometer (Krüss GmbH, Hamburg, Germany). A J-KEM (SYR-1200, J-KEM Scientific, St. Louis, MO) micro-syringe pump was used to dispense the air bubbles. A schematic of the instrument is depicted in Fig. 1. The apparatus was mounted on a vibration-isolated table and equipped with manufacturer-supplied programs using an axi-symmetric drop or bubble shape analysis algorithm to calculate the ST between air and aqueous phase from a captured drop or bubble images. The program provided fast (maximum 3 readings per second), accurate, and repeatable [standard deviation (SD) =  $\pm 0.1$  mN/m] real-time ST values. We used two different configurations for ST measurements: a pendant drop configuration and a sessile-bubble configuration. The former configuration was used only for blister pack solutions. A drop of liquid was made

**TABLE 1.**  
SCL materials and specifications; ST of packaging solutions

Lens brand name (abbreviation)	Material (manufacturer)	Surface treatment	% H <sub>2</sub> O	Lens specifications power (D)/diameter (mm)/base curve radius (mm)	ST of packaging solutions mean $\pm$ SD (mN/m)
Acuvue 2	Etafilcon A (Vistakon)	None	58	−1.00/8.7/14.0	53.5 $\pm$ 1.8
Biomedics 55 Premier	Ocufilcon D (Cooper Vision)	None	55	−1.00/8.6/14.2	41.6 $\pm$ 1.5
Extreme H <sub>2</sub> O	Hioxifilcon D (Hydrogel Vision)	None	54	−1.00/8.6/14.2	37.9 $\pm$ 0.7
Proclear	Omafilcon A (Cooper Vision)	None	62	−1.00/8.6/14.2	59.8 $\pm$ 2.5
AirOptix Night&Day	Lotrafilcon A (Ciba Vision)	None, (Aqua Moister)	24	−1.00/8.6/13.8	68.1 $\pm$ 1.0
Accuvue Advance	Galyfilcon A (Vistacon)	None, (Internal PVP)	47	−1.00/8.7/14.0	58.5 $\pm$ 2.3
Accuvue Oasys	Senofilcon A (Vistacon)	None, (Internal PVP)	38	−1.00/8.8/14.0	46.5 $\pm$ 1.5
Biofinity	Comfilcon A (Cooper Vision)	None	48	−1.00/8.6/14.0	44.5 $\pm$ 0.4
Focus Night&Day	Lotrafilcon A (Ciba Vision)	Plasma coating	24	−1.00/8.6/13.8	66.5 $\pm$ 0.6
O <sub>2</sub> Optix	Lotrafilcon B (Ciba Vision)	Plasma coating	33	−1.00/8.6/14.2	70.3 $\pm$ 0.6
PureVision	Balafilcon A (Bausch&Lomb)	Plasma oxidation	36	−1.00/8.6/14.0	70.0 $\pm$ 0.2

**FIGURE 1.**

Schematic of the sessile-captive bubble tensiometer-goniometer setup.

at the tip of a stainless steel needle connected to a syringe, then the needle was fixed inside an optical cell containing a small amount of a surfactant-free solution (e.g., Opti-Free or OF) and sealed to reduce drop evaporation. In the sessile-bubble configuration, an air bubble, formed by dispensing air through a hole drilled in the Teflon rod as depicted in Fig. A2 (Appendix; see Supplemental Digital Content 1, <http://links.lww.com/ACADMED/A15>), was immersed vertically into a cell filled with aqueous media. The details of the sessile bubble configuration<sup>22,23</sup> and some aspects of wettability dynamics have been published elsewhere.<sup>24–26</sup> Distilled and deionized water was used as a standard for reference purposes for both pendant drop and sessile bubble configurations. The ST of water, which is a constant physical characteristic of pure liquid, measured under both configurations was  $72.4 \pm 0.15$  mN/m in excellent agreement with the reference value of pure water at 22°C.

Because of the limited volume of blister pack solutions, typically 1 ml or less, only the pendant drop configuration was used for ST measurements. Each individual blister pack solution was tested separately. The measurements were conducted at an ambient temperature of  $22 \pm 1^\circ\text{C}$ , and repeated three to five times.

Before CA and ST measurements, the ST of the OF lens care solution from more than 30 randomly selected bottles was measured. The mean and SD of ST was  $71.5 \pm 0.5$  mN/m for each

bottle and remained constant up to 24 h, indicating that OF solutions were surfactant free because this value of the ST was close to ST of pure water, 72.5 mN/m, at the same temperature.

### Lens Preparation Protocol

Lenses were removed from their blister packs by gently pulling them out with stainless steel “Duck Bill” flat nose tweezers while holding the lenses at their very edge. Each lens was then rinsed copiously with OF solution. Excess rinsing solution was quickly and gently drained by touching the lens edge with a fresh piece of filter paper (Fisher Scientific, Pittsburgh, PA). The lens was immediately placed in an optical glass vial,  $30 \times 30 \times 40$  mm, (Hellma Cells, Inc., Plain View, NY) containing 15 to 20 ml of OF solution. The entire procedure of lens rinsing and draining took no more than a few seconds, thus ensuring minimal lens dehydration.<sup>27</sup> Once immersed into the cell filled with OF solution, the lens was carefully centered on top of the lens holder with its anterior surface facing up and out toward the aqueous phase. The cylindrical cap of the lens holder was gently lowered on top of the lens and pressed down to hold the lens immobilized in the holder. Special care was taken to retain centering of the lens on the lens holder and to avoid possible air bubble entrapment between the

lens and lens holder. A detailed drawing (Fig. A1) and description of the custom-made lens holder are provided in Appendix. A minimum of five lenses of each brand was tested.

CA and ST were measured immediately after the lens was removed from its blister pack (baseline or day 0) and measurements were repeated after soaking (day 1 or 7). After baseline measurements, each lens was placed into a clean scintillation glass vial containing 20 ml of OF solution. The vials containing the lenses were then placed into a shaker (MaxQ2000, J-KEM Scientific, St. Louis, MO) and were agitated at a speed of 100 rpm overnight, typically for 16 to 18 h. This procedure was repeated for 7 consecutive days and each day OF solution was replaced with fresh solution after overnight lens soaking. The soaking of the lenses in surfactant-free OF was performed to remove (leach out) the surface-active ingredients of the blister pack solution accumulated in the lens matrix and thus set apart the effect of these substances on the lens surface wetting properties from the inherent wettability of the lens material itself.

All manipulations of lenses, soaking solutions, and glassware were conducted using powder-free nitrile gloves to avoid contamination. Glassware, lens holders, and bubble holders were cleaned by soaking for 30 min, first in 3% HCl solution, then in saturated KOH in 95% ethanol solution, followed by a thorough rinsing with distilled and deionized water.

### Contact Angle Measurements

A Kruss tensiometer was equipped with an option for CA measurements using either sessile drop or captive bubble configurations. With the standard software supplied by the manufacturer, these measurements could be conducted only on flat solid substrates. Customized software was required to measure CAs on a curved lens surface.<sup>16,18</sup> In our experiments, an in-house LabView program was developed to perform real-time CA and contact point position data acquisitions.<sup>19,20,28–30</sup> The program captured images of an air bubble in contact with a lens (Fig. 2a), extracted profiles of both lens and bubble, and then fit these profiles with fourth-order polynomials (Fig. 2b). The contact point position, denoted as “X” in Fig. 2b, was determined from extrapolation of

these fits to the point of intersection, and the CAs were calculated from fit tangents. Thus, data collection and treatment were completely computerized, excluding any kind of operator-dependent manual fit.<sup>16,18</sup> At the magnification of 1 mm = 140 pixels used for detection of contact line position and the advancing and receding CA determination, the accuracy was  $\pm 0.01$  mm and  $\pm 1.0^\circ$ , correspondingly.

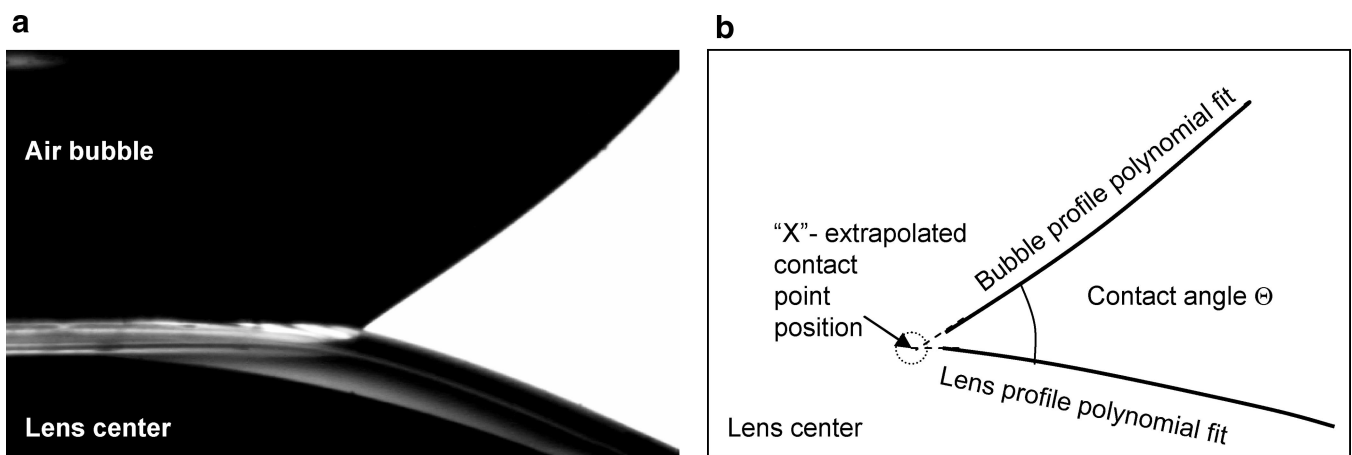
The schematics and details of the bubble and lens holder designs, procedures for bubble-lens apex alignment, and other experimental procedures are described in the Appendix.

### Statistical Analysis

Repeated measures analysis of variance was used to assess the differences in CA, ST, and adhesion energy between lens groups and across days for conventional hydrogels and SiH lenses. Post hoc multiple pair-wise comparisons using the Tukey HSD method determined which pairs of lenses differed significantly from each other.

### RESULTS

The STs of the blister pack solutions from the different lens brands are reported in Table 1. Most of the blister pack solutions had ST lower than that of pure water (72.5 mN/m) or OF solution (71.2 mN/m), indicating that they contained surface-active ingredients. These additives could penetrate into the lens matrix during storage and leach out and subsequently be washed away during lens wear. As a result, the initial wettability of a pristine lens (i.e., a fresh lens removed from its blister pack) might be altered during wear because of the loss of these surfactants. We therefore examined the effect of surface-active ingredients released from SCLs on lens surface wettability after repetitive overnight soaking in surfactant-free media. Soaking in surfactant-free OF was used to remove surface-active additives from the lenses so that the intrinsic wettability (i.e., the wettability of lens material itself in the absence of surface-active substances) could be evaluated. The means and SDs of CA, ST, and adhesion energy, stratified by Day and lens type, are summarized in Table 2. CA data from day 1 are also provided in addition



**FIGURE 2.**

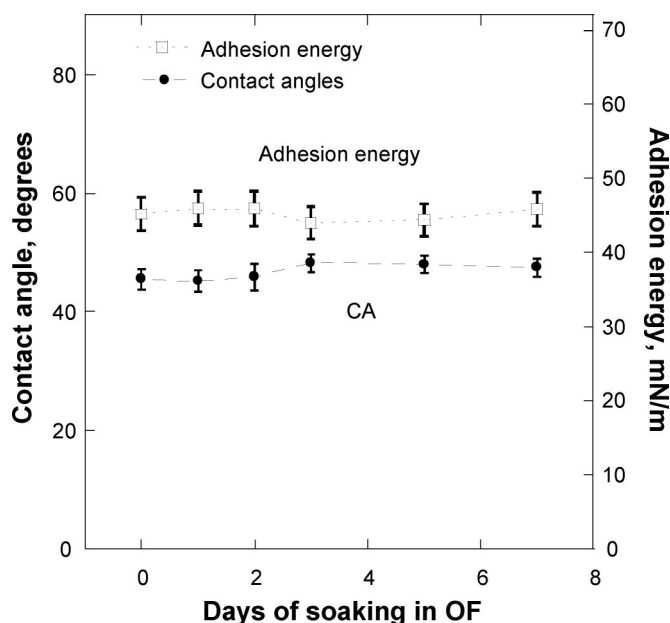
a, Captured image of the air bubble in contact with an SCL. b, Schematic of the computer-generated lens and bubble profile polynomial fits used for CA calculation.



**TABLE 2.**

Summary of CAs, ST, and adhesion energy values for different lens brands at days 0, and after days 1 and 7 of soaking in surfactant-free solution

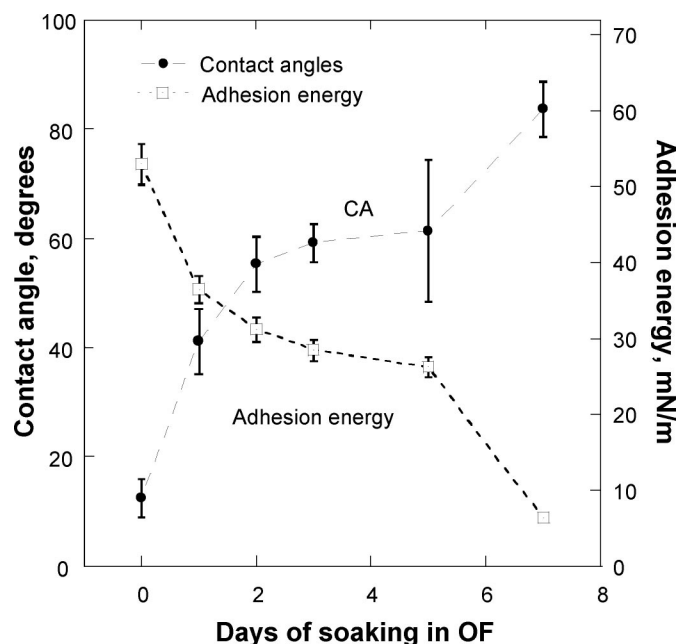
Lens brand	ST [mN/m] Mean $\pm$ SD		CA [°] Mean $\pm$ SD			Adhesion energy [mN/m] Mean $\pm$ SD	
	Day 0	Day 7	Day 0	Day 1	Day 7	Day 0	Day 7
Acuvue 2	44.43 $\pm$ 6.23	58.25 $\pm$ 3.45	10.88 $\pm$ 3.06	56.58 $\pm$ 24.02	83.73 $\pm$ 4.51	43.55 $\pm$ 6.41	8.68 $\pm$ 2.27
Biomedics 55 Premier	53.17 $\pm$ 2.02	59.07 $\pm$ 6.93	35.83 $\pm$ 11.27	44.90 $\pm$ 15.71	71.18 $\pm$ 6.92	43.83 $\pm$ 8.32	17.77 $\pm$ 7.71
Extreme H <sub>2</sub> O	60.5 $\pm$ 3.80	65.1 $\pm$ 1.81	48.5 $\pm$ 7.42	51.77 $\pm$ 2.94	57.6 $\pm$ 9.06	40.42 $\pm$ 8.43	34.88 $\pm$ 8.78
Proclear	57.33 $\pm$ 7.83	63.00 $\pm$ 7.42	55.60 $\pm$ 13.43	47.40 $\pm$ 7.50	79.70 $\pm$ 8.13	31.70 $\pm$ 12.72	11.74 $\pm$ 9.60
Air Optix Night&Day Aqua	57.18 $\pm$ 5.65	63.50 $\pm$ 2.71	17.00 $\pm$ 7.39	22.8 $\pm$ 7.38	30.06 $\pm$ 3.77	54.19 $\pm$ 3.87	54.80 $\pm$ 1.10
Acuvue Advance	47.75 $\pm$ 2.91	62.55 $\pm$ 3.35	34.94 $\pm$ 3.53	29.90 $\pm$ 11.17	26.65 $\pm$ 13.77	39.30 $\pm$ 4.27	54.00 $\pm$ 8.46
Acuvue Oasys	49.13 $\pm$ 4.63	62.73 $\pm$ 3.72	16.43 $\pm$ 7.49	19.27 $\pm$ 9.32	27.73 $\pm$ 5.31	47.68 $\pm$ 3.87	54.32 $\pm$ 4.36
Biofinity	52.03 $\pm$ 5.54	63.13 $\pm$ 6.93	12.80 $\pm$ 4.49	9.30 $\pm$ 4.81	20.88 $\pm$ 9.33	50.38 $\pm$ 4.86	58.30 $\pm$ 5.95
Focus Night&Day	64.45 $\pm$ 2.84	67.88 $\pm$ 0.64	42.78 $\pm$ 4.37	48.50 $\pm$ 4.81	42.53 $\pm$ 5.22	47.15 $\pm$ 2.64	49.83 $\pm$ 3.76
O <sub>2</sub> Optix	60.00 $\pm$ 6.10	66.93 $\pm$ 2.11	35.93 $\pm$ 2.38	44.67 $\pm$ 2.74	48.70 $\pm$ 3.75	48.53 $\pm$ 4.51	44.16 $\pm$ 4.54
PureVision	60.13 $\pm$ 11.86	67.08 $\pm$ 0.70	82.95 $\pm$ 15.08	76.70 $\pm$ 2.15	74.40 $\pm$ 9.34	14.49 $\pm$ 28.49	17.79 $\pm$ 10.23

**FIGURE 3.**

CA and adhesion energy as functions of soaking time for the Focus Night&Day lens.

to the CAs taken on day 0 and day 7. It is apparent that for most lenses, 1 day of soaking was not sufficient to deplete surfactants.

Figs. 3 and 4 depict results for two lens types—Focus Night and Day, which has low water content and does not have surfactants in its blister packaging solution, and Acuvue 2, which is made of highly porous material and uses a packaging solution loaded with surface-active substances. Specifically, Fig. 3 shows that the wettability of Focus Night & Day (preAqua formulation) lenses remained nearly the same before and after soaking, in accordance with the data of Table 1, confirming that this lens brand had no surfactants in its blister pack solution. The small difference in ST between the Focus Night & Day blister pack solution and a reference liquid (water) is likely due to the presence of some organic

**FIGURE 4.**

CA and adhesion energy as functions of soaking time for the Acuvue 2 lens.

impurities, such as hydrogel monomers or oligomers leaching from lens material during prolonged storage in blister pack. In Fig. 3, the CAs and adhesion energies (numerically equal to the product of CA cosine and ST) are plotted as functions of soaking time. Each CA point corresponds to an average value of up to 100 CA measurements, performed according to the procedure described in the Appendix; the vertical bars show SDs.

Fig. 4 shows the wettability results for Acuvue 2 lenses measured according to the identical study protocol—CA and ST measured at day 0 and after soaking in OF for up to 7 days. In contrast to Focus Night & Day lenses, the CA of Acuvue 2 lenses grew significantly after each overnight soaking and, correspondingly, the adhesion

energy was reduced from 53.0 mN/m at day 0 to 6.4 mN/m after soaking for 7 days, indicating that lens wettability was reduced by depletion of surface-active agents.

Repeated measures analysis of variance was performed separately for conventional hydrogels and SiH lenses. For conventional hydrogels lenses, the results showed that the overall differences in CA values between lens brands were significant ( $p < 0.001$ ); after adjusting for multiple comparisons, only the Tukey HSD between Acuvue 2 and Proclear lenses was statistically significant ( $p < 0.001$ ). The interaction between days of soaking and lens brand was not significant ( $p = 0.091$ ), although this may be due to small sample sizes, as suggested by the apparent differences between brands listed in Table 2. For pristine Acuvue 2 lenses, the ST at day 0 was low, then increased to a high level at day 7. For Biomedic 55, Extreme H<sub>2</sub>O, and Proclear lenses, most tested lenses started with mid-range ST at day 0 and increased slightly at day 7. There was a significant decrease overall in adhesion energy between day 0 and day 7 ( $p < 0.001$ ). There were not significant differences among lens brands overall. There was, however, a significant interaction between day and lens brand ( $p = 0.001$ ), indicating that the magnitude and direction of the change in adhesion energy after 7 days of soaking differed among the brands of conventional lenses examined in this study.

The advancing CA on SiH lenses did not increase much after 7 days of soaking. Indeed, there was not a significant overall change in CA between day 0 and day 7 ( $p = 0.092$ ). However, there were significant differences among lens brands overall ( $p < 0.001$ ), and a significant interaction between day and lens brand ( $p < 0.001$ ), indicating that the different lens brands showed different patterns of change over 7 days of soaking in OF solution. Acuvue Oasys, Biofinity, and O<sub>2</sub> Optix all increased slightly in CA after soaking, whereas Focus Night & Day lenses remained unchanged. Interestingly, Acuvue Advance, Air Optix Night & Day Aqua, and PureVision lenses all decreased slightly in CA after 7 days. PureVision lenses exhibited a high CA overall, whereas Acuvue Advance, Acuvue Oasys, Air Optix Night & Day Aqua, and Biofinity lenses exhibited a low CA overall. After adjusting for multiple pair-wise comparisons, the Tukey HSDs showed PureVision to be significantly different from each of these other four lens brands. Focus Night & Day and O<sub>2</sub> Optix were intermediate in CA between PureVision and the other SiH lens brands after soaking.

For the SiH lenses, there was a significant difference in adhesion energy between day 0 and day 7 overall ( $p = 0.002$ ), although the magnitude of the change in adhesion energy after soaking was much less than for conventional hydrogels lenses. There was a significant difference among lens brands in overall adhesion energy ( $p < 0.001$ ), and post hoc pair-wise comparisons show that PureVision lenses exhibited significantly lower adhesion energy than all other SiH brands.

At day 0, all SiH lenses except Acuvue Advance and PureVision had aqueous adhesion energy higher than that exhibited by conventional hydrogels lenses, and after leaching of surface-active agents by soaking, all SiH lenses except PureVision had aqueous adhesion energy higher than that exhibited by conventional hydrogels lenses, indicating better wettability of SiH lenses. For all SiH lenses except AirOptix Night&Day Aqua and O<sub>2</sub>Optix lenses, adhesion energy increased slightly after 7 days of soaking in surfactant-free solution. Although of modest magnitude, these changes indicate that the wettability of the SiH lenses was actually enhanced after

soaking in OF, as opposed to the aqueous adhesion energy reduction and wettability decline observed for most conventional lenses after depletion of surface-active ingredients. It is important to note that the receding CAs for all studied lenses were similar in value (mean  $\pm$  SD =  $12^\circ \pm 5^\circ$  for both conventional and SiH lens types) and were not affected by the presence of surfactants.

## DISCUSSION

CA values are often reported in the marketing literature (e.g., packaging inserts) as a proof of good (or bad) lens surface wettability. However, it has been recognized that a standard technique for CA measurement has not yet been established, and that the validity of many reported data should be seriously questioned.<sup>18</sup> In the scientific literature, one can find great divergence or disagreement between CAs measurements for the same lens brand using different techniques and different aqueous media.<sup>16,18,20,30</sup> For instance, measured by the captive bubble technique, advancing CAs for PureVision lenses were reported to be  $80^\circ$ ,<sup>20</sup>  $93.6^\circ$ ,<sup>28</sup>  $101^\circ$ ,<sup>18</sup> and  $\sim 110^\circ$ ,<sup>31</sup> compared to as high as  $120^\circ$  estimated by the sessile drop method.<sup>32</sup> The advancing CA of  $120^\circ$  for the plasma-oxidized surface of PureVision lenses does not appear to be physically plausible. It is only  $6^\circ$  lower than the  $126^\circ$  found for Teflon,<sup>26</sup> the most hydrophobic synthetic polymer known. These discrepancies cause substantial confusion and clearly indicate that these measurements were largely dependent on the methods and conditions used. It is worth noting that in all the articles cited above, the ST of the aqueous medium brought into contact with a lens surface was not taken into account in the assessment of lens-surface wettability.

This work focused on modifying the current captive-bubble technique for reliable and physically plausible SCL surface wettability evaluations under dynamic-cycling conditions, mimicking blinking cycles in the eye. In accordance with the modern theory of wetting phenomena, special attention was paid to ST variations during the course of the experiments. We argue that CA measurements alone are not sufficient to obtain a physically meaningful surface-wettability evaluation. Only in combination with the ST of the aqueous phase in contact and equilibrated with the SCL surface will CA values form a set of parameters satisfying the thermodynamic requirements. In our experiments, all CA measurements were performed in conjunction with concurrent measurements of the ST at the air-aqueous interface.

We demonstrated that for most of the conventional SCLs examined in this study, there were surface-active ingredients present in the blister-pack solutions that led to a noticeable and positive effect on their initial wettability as gauged by adhesion energy *in vitro*. The adhesion energy values of Acuvue 2, Biomedic 55, Extreme H<sub>2</sub>O and Proclear lenses were found to be higher on removal from the blister packs than after soaking in OF for 7 days, at which point most of the surface-active agents had leached out from the lens matrix. These data suggest that the wettability of these conventional hydrogels lenses was surfactant-dependent, and that the presence of surface active wetting agents in the blister pack solutions was necessary to improve the initial lens surface wettability.

As gauged by the aqueous adhesion energy, an improvement in surface wettability on prolonged soaking in surfactant-free media was demonstrated for most of the SiH lenses. For these lenses,

small but statistically significant changes in the advancing CAs and the STs were observed during a week of soaking in a surfactant-free solution. Even though the advancing CAs increased slightly in most cases, the aqueous adhesion energy values became higher due to greater ST after lens-bubble equilibration. For O<sub>2</sub>Optix and Air Optix Night&Day Aqua lenses, however, slight increases in the advancing CAs and decreases or no change in the aqueous adhesion energies were observed after prolonged soaking. For these lenses, the loss of surface-active ingredients had a minor negative effect on surface wettability, which was, small in comparison with that observed for conventional hydrogel lenses. Furthermore, most of the pristine SiH lenses (except PureVision) have relatively high aqueous adhesion energy when compared with conventional SCLs. The wettability of SiH lenses was sustained or even improved after prolonged soaking in OF. These observations suggest that the wettability of the SiH lenses measured in our experiments was a self-sustained property of their surfaces. The high surface wettability of SiH lenses was preconcerted by either lens surface treatment such as plasma oxidation (Focus Night&Day, PureVision) or by built-in lens-matrix surface-modifiers (Acuvue Oasys and Acuvue Advance), rather than being dependent on external (blister pack solution) wetting agents as was found for conventional hydrogel lenses.

We strongly believe that the aqueous adhesion energy values, calculated according to Young Eq. 1, provide valuable and physically meaningful information regarding the wettability of soft lens surfaces. Often in previous studies, the surface wettability of different lenses was compared using CA measurements conducted in different aqueous media with varying and unknown STs. The aqueous adhesion energy provides a thermodynamically defined scale for the evaluation and comparison of solid-surface wettability measured under different experimental conditions. The other important thermodynamic parameter for gauging the wetting of a solid by a liquid is the spreading parameter, or spreading coefficient  $S^{15}$  defined as

$$S = (\gamma_{sv} - \gamma_{sl}) - \gamma_{lv}, \quad (2)$$

where  $\gamma_{sv}$  is the ST of a solid surface against a gas phase (liquid vapor),  $\gamma_{sl}$  is an interfacial tension between liquid and solid phases, and  $\gamma_{lv}$  is the ST of a liquid in equilibrium with its vapor. When the spreading coefficient is positive, the liquid wets the solid surface completely, spreading spontaneously over the solid surface with 0 CA. When  $S < 0$ , the liquid exhibits partial wetting, forming a drop or contact line with a CA defined by Young Eq. 1. As one can see by comparing Eqs. 1 and 2, the adhesion energy of a solid surface brought into contact with a liquid has to be higher than the ST of that liquid to sustain a positive spreading coefficient for each particular liquid-solid combination. Eq. 2 has an important practical implication, namely, that it sets a boundary for the aqueous adhesion energy value above which complete spreading of a liquid over a solid surface should be expected. Thus, the thermodynamics predict that for a contact lens with intrinsic aqueous adhesion energy above the ST of human tears, which is approximately 40 mN/m,<sup>33,34</sup> one should expect that the tear fluid will wet a lens surface completely when a lens is placed on the eye. Complete wetting and tear-film spontaneous spreading with 0 CA should be observed on the lens for at least some period of time during which

the lens-surface retains its original adhesion energy. Note that adhesion energy is likely to be changed due to interaction with the tear constituents. There are indications in the literature<sup>20</sup> that some model tear proteins, such as lysozyme and mucin, cause substantial reduction of the *in vitro* advancing CAs on SCLs.

It is important to note that the receding CAs for all lenses studied were similar in value (mean  $\pm$  SD =  $12^\circ \pm 5^\circ$  for both conventional and SiH lens types) and were not affected by the presence of surfactants. That is hardly surprising, because for highly porous contact lens materials, containing at least 25% and up to 75% water, there is a strong interaction between the water residing in the pore openings on the lens surface and the receding aqueous phase. The hydrophilic parts of a lens surface attract and retain water as the aqueous phase recedes over the lens surface, which inevitably leads to the low values of dynamic receding angle. CA hysteresis on a soft lens surface is related to the chemical heterogeneity of the porous lens surface. In the water advancing process, one starts with a lens surface on which the aqueous film has ruptured, causing the lens surface to be in direct contact with the air. The advancing water has to displace the air to move over exposed hydrophobic polymeric patches on the lens surface, which resists being covered by water, preferring to remain covered by the air. To move over these water-repelling patches, the aqueous front has to form a high advancing angle before the water starts to slide over and form a film covering these hydrophobic patches. Once the water film is ruptured and the hydrophobic surface is exposed to air, it requires extra energy (thus, a higher CA) to displace the air and form a continuous aqueous film on the surface.

The question of how *in vitro* lens-surface wettability is related to clinical contact lens performance, *in vivo* tear film stability, and subjective comfort ratings remains unanswered. Preliminary results have shown no correlations among these parameters for asymptomatic soft lens wearers.<sup>35</sup> However, a larger sample size is required to confirm this finding. The relationships among lens initial *in vitro* and *ex vivo* wettability (advancing CAs), clinically evaluated lens wettability *in vivo*, and non-invasive tear film stability in conjunction with comfort ratings by contact lens wearers (asymptomatic and symptomatic) will be addressed in forthcoming articles.

Some clinically relevant recommendations can be made based on the *in vitro* results reported here. It was found that SiH lenses do not significantly change their surface properties on soaking in a surfactant-free medium. In fact, some of the SiH lenses exhibited better surface wettability after depletion of surfactants. It would be reasonable to suggest that patients with issues of hyper-sensitivity or intolerance to the “soapy” ingredients of the blister pack solutions might benefit from thorough rinsing of the lenses with a surfactant-free saline solution (e.g., Unisol4 or SoftWear) before insertion. It is also conceivable that one can remove irritating ingredients by disinfecting and soaking SiH lenses overnight in a surfactant-free lens care solution such as AOSept (CIBA) before the first use of a lens, which could be beneficial to patients with sensitive eyes.

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## APPENDIX

The appendix is available online at <http://links.lww.com/ACADMED/A15>.

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